

Ion Chemistry of the Stratosphere

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The study of the ion chemistry of the earth's atmosphere began with the ionospheric E and F layers, which are located above 90 km (Figure 1). The first studies utilized reflection of radio waves from the electrons in these regions and then, with the advent of the rocket and satellite era, in situ ion composition measurements. The complexity of the ion chemistry increases as the altitude decreases. Above ~120 km the low ambient pressure allows direct sampling into mass spectrometers on rockets and satellites. Above ~150 km satellites are capable of making observations of properties relevant to ion chemistry, e.g., solar ionizing UV spectra, neutral composition and temperature, electron density, and air-glow emission, as well as the ion composition. This has permitted detailed analyses of the ion chemistry to be made. The simple nature of the neutral composition at high altitude, largely O, O₂, N, N₂, He, and H, greatly simplifies the ion chemistry.

The chemistry of the major ion species above ~120 km is now well-understood.¹ This has been facilitated by comprehensive measurements obtained with the Atmosphere-Explorer-C satellite and detailed laboratory measurements of ion processes. The direction of upper ionospheric chemical research now is concentrated on the chemistry of trace ions. This includes doubly charged ions and metastable excited ions, which can be analyzed with the Atmosphere-Explorer data and new laboratory reaction rate measurements. In some cases the laboratory rate constants are beyond present measurement capability, and the analysis of in

situ ion composition data yields the only available reaction rate data.

Below ~90 km, the ion chemistry of the atmosphere becomes much more complex. It is in this altitude range that a transition from "low" pressure to "high" pressure ion chemistry occurs. The higher pressure and low temperature lead to a more important role for three-body reactions relative to the binary reactions which dominate at higher altitude. Weakly bound cluster ions occur in substantial concentrations and play an important role as intermediates in reaction sequences. The attachment of electrons, a high-pressure phenomenon, leads to a very complex negative ion chemistry. An abundance of chemically reactive trace polyatomic molecules whose absolute concentrations become significant is involved in the chemistry.

The ion chemistry of the D region, ~60–90 km, has been studied by means of rocket-borne mass spectrometers since the initial measurement in 1963 of Narcisi and Bailey.² A detailed qualitative outline of the positive and negative ion chemistry has been developed from laboratory measurements.¹ However the lack of a stable sampling platform in which all of the relevant parameters can be simultaneously measured has precluded a detailed quantitative understanding of D-region ion chemistry. An indication of the complexity of the problem is manifested in the large variability from one observation to another of ion composition, especially for negative ions. The indications to date are that our present positive ion reaction scheme may be essentially correct (although quantitatively incomplete) and that our present negative ion reaction scheme is probably missing important reaction processes. There is current progress occurring in both in situ measurements and in laboratory reaction studies of D-region ion chemistry. Progress will probably be slow but steady in this field for many years.

Figure 1 shows a schematic total ion concentration profile in the atmosphere. The boundaries of the al-

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(1) E. E. Ferguson, F. C. Fehsenfeld, and D. L. Albritton, "Ion Chemistry of the Earth's Atmosphere", "Gas Phase Ion Chemistry", Vol. 1, M. T. Bowers, Ed., Academic Press, New York, 1979, Chapter 2.

(2) R. S. Narcisi and A. D. Bailey, *J. Geophys. Res.*, **70**, 3687 (1965).

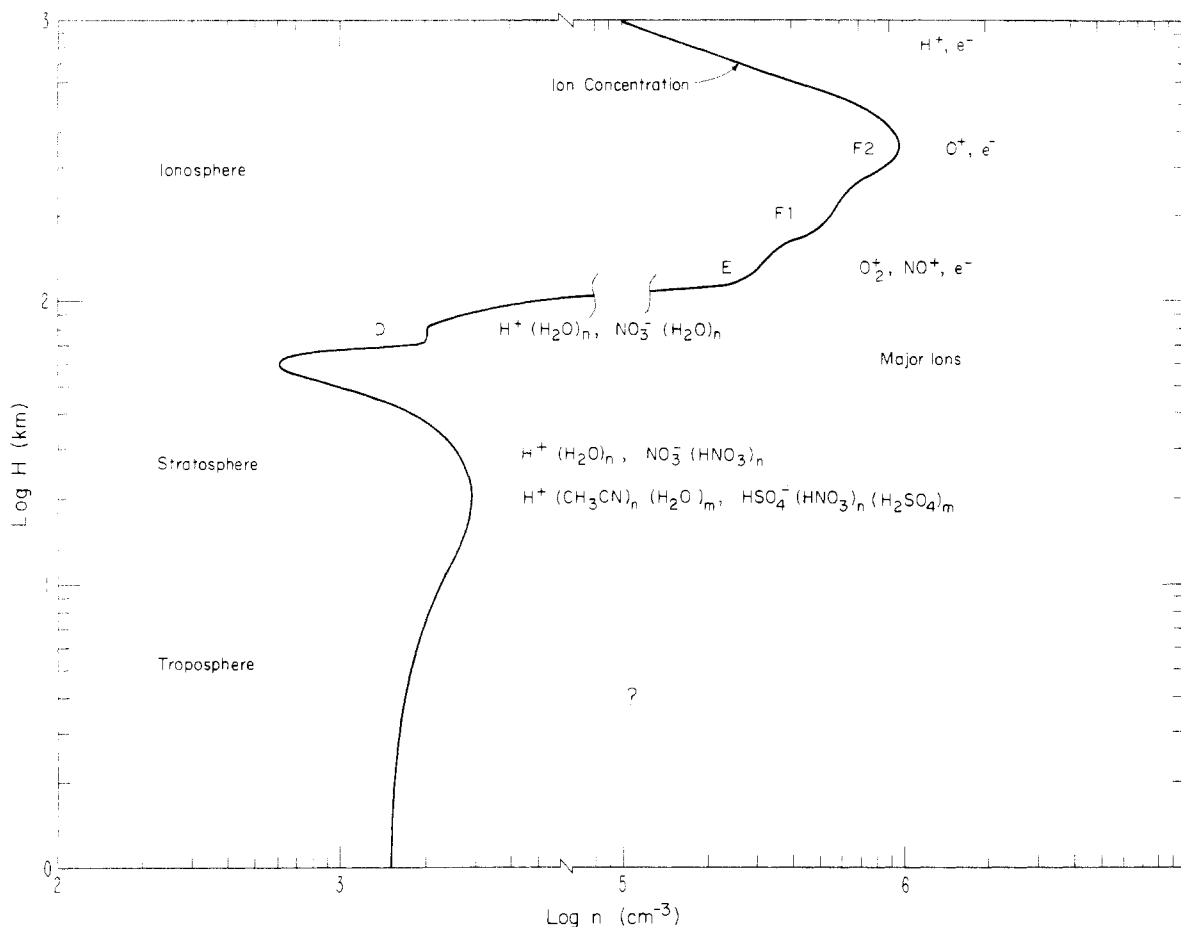


Figure 1. Schematic ion concentration profile in the earth's atmosphere.

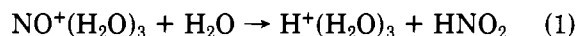
titude regimes are variable in time and space, as are the ion densities. There are systematic variations of ion density with time of day, latitude, and solar activity. The troposphere and stratosphere are defined from a meteorological viewpoint as regions of decreasing and increasing temperature with altitude. The ionospheric D, E, F1, and F2 regime nomenclature is historical in origin and is based on radio wave reflection observations.

In the E and F regions the ionization source is mainly solar ultraviolet photoionization of O, N₂, and O₂. The positive ions are balanced by free electrons and their mutual loss is by dissociative recombination of molecular ions and electrons. In the stratosphere and troposphere ionization results mainly from high-energy galactic cosmic rays impinging on the earth. The positive ions are balanced by negative ions and their mutual loss is due to neutralizing collisions. The D-region is a transition region in which the dominant ionization is photoionization of the trace species NO by the intense solar Lyman α line of atomic hydrogen. Dominant ion species of the various regions are indicated in Figure 1.

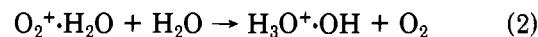
In this Account we consider current advances in the ion chemistry of the stratosphere (~10–50-km altitude) for which the first observations have only recently been obtained. The ion chemistry of the stratosphere has been studied as a logical extension of D-region ion chemistry. The wealth of laboratory data on D-region processes has been utilized and extended to allow for the additional neutral species present in the stratosphere.

Stratospheric Positive Ion Chemistry

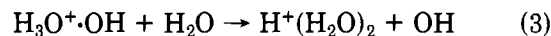
In the D-region proton hydrates (PH's) are observed to be dominant ions, in many observations, and their origin has been explained^{3,4} as a consequence of hydration of NO⁺, and to lesser extent O₂⁺, followed by the reactions



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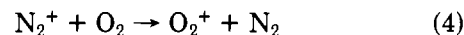


Reaction 2 is rapidly followed by



The hydration of NO⁺ involves association with N₂ and CO₂ which are then displaced by H₂O molecules in ligand switching reactions which typically occur at the collision rate when exothermic.⁵

In the undisturbed stratosphere (and also in the troposphere, the lowest 10–15 km of our atmosphere) where the dominant ionization source is galactic cosmic radiation, O₂⁺ is produced directly and indirectly by charge transfer.



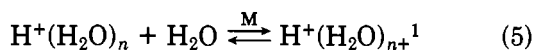
A typical ionization rate is ~10 ion pairs cm⁻³ s⁻¹ in the

(3) E. E. Ferguson and F. C. Fehsenfeld, *J. Geophys. Res.*, **74**, 5743 (1969).

(4) F. C. Fehsenfeld and E. E. Ferguson, *J. Geophys. Res.*, **74**, 2217 (1969).

(5) N. G. Adams, D. K. Bohme, D. B. Dunkin, F. C. Fehsenfeld, and E. E. Ferguson, *J. Chem. Phys.*, **52**, 3133 (1970).

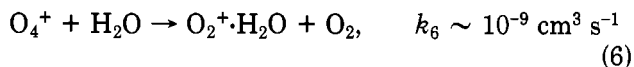
stratosphere. Solar disturbances can lead to greatly enhanced ionization rates due to solar protons, particularly in the upper stratosphere. Reactions 2 and 3 lead rapidly (in the order of milliseconds) to PH's which rapidly assume a quasi-equilibrium distribution



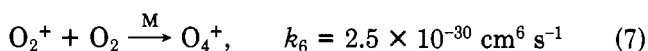
The processes implied by (5) are rapid compared to the overall PH lifetime which is $\sim 10^4$ s and is determined by PH recombination with ambient negative ions. The balance of ion production and loss for typical undisturbed solar conditions (day or night) is an ion density of the order of $\sim 10^3$ ions cm^{-3} in the stratosphere, relatively insensitive to altitude.

In order to extend D-region positive ion chemistry into the stratosphere, we pose two questions: (1) Will the PH's still be formed, or do stratospheric species exist which will interfere with their production? (2) If the PH's are formed, do stratospheric species exist with which they will then react, leading to more stable positive ions?

The possibilities for disrupting PH formation are very restricted because of the short time scale. The species $\text{O}_2^+\cdot\text{H}_2\text{O}$ is produced largely by the reaction

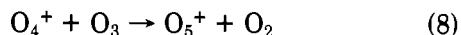


which occurs in every collision. The O_4^+ is produced by



which is extremely rapid because of the large O_2 concentration. Reactions 2 and 6 are slower than reaction 7 and hence rate controlling. Since (2) and (6) occur with large rate constants, it follows that in order for any species to interfere, it must have a concentration comparable to that of water, i.e., a few parts per million.

The only species this abundant in the stratosphere are CO_2 , CH_4 , and O_3 . The chemistry of these species has been investigated⁶ and found not to disrupt the conversion to PH's. The role of O_3 is of interest since (8) is fast, $\sim 10^{-9} \text{ cm}^3 \text{ s}^{-1}$,



The O_5^+ ion mass 80⁺, has probably been observed at higher altitudes, although it was not identified as such. Because of (8) one must also consider possible reactions of O_5^+ . CO_2 has no reactivity: it can displace O_2 in O_4^+ in a reaction approximately thermoneutral, but this would have no effect since H_2O would rapidly displace CO_2 clustered to O_2^+ . Methane is a potentially significant reactant, since exothermic reactions of O_2^+ , O_3^+ , and O_4^+ exist. However in every case these reactions are very slow and noncompetitive. It thus appears certain the PH's will be produced in the stratosphere and probably also in the troposphere where the H_2O concentration is much larger.

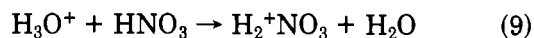
Therefore we turn to the second question, are there stratospheric species which can react with the PH's? The concentration constraints are very much less restrictive here because of the long ion lifetimes. In order to acquire a reaction rate equal to the inverse lifetime,

$\sim 10^{-4} \text{ s}^{-1}$, for a species with a large ($\sim 10^{-9} \text{ cm}^3 \text{ s}^{-1}$) rate constant, a concentration of only $\sim 10^5 \text{ cm}^{-3}$ is required. When one realizes that ions of only a percent or less abundance can be detected, it is obvious that ion composition measurements have potential for extremely sensitive analytical detection of atmospheric trace species, essentially functioning as an in situ passive chemical ionization mass spectrometry method. Measurements of concentrations as low as 10^{-15} mixing ratios can be realized.

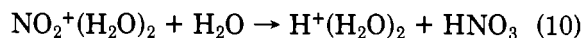
A restrictive constraint on the nature of the species which might react with PH's that keeps the problem tractable is the reaction energetics. It is necessary that a reaction be exothermic in order to occur. The PH's are very stable chemically, which is why they are the terminal species in ionized moist air. The recombination energy of H_3O^+ , for example, is only 6.4 eV, and this decreases rapidly with hydration. It is unlikely that any species in significant concentration in the stratosphere have ionization potentials low enough to transfer electrons to proton hydrates. For example, metals such as sodium, if present in the gas phase, will quickly combine into stable compounds.

The most favorable circumstance for reactivity with PH's is the presence of molecules with large proton affinities, i.e., larger than H_2O which is 7.2 eV (170 kcal mol^{-1}). Ionization potential and proton affinity are not unrelated of course; the low ionization potential of sodium, for example, implies that its compounds (such as NaOH , NaCl , and NaNO_3) will all have large proton affinities.

There are abundant and well-known stratospheric compounds with large proton affinities. The most prominent is HNO_3 , which is known to occur in the ppb concentration range. The reaction

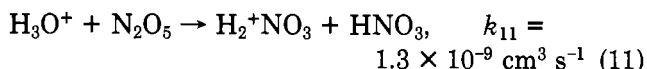


is found⁷ to occur rapidly, $k_9 \sim 10^{-9} \text{ cm}^3 \text{ s}^{-1}$, and also to occur when there are more waters of hydration on the proton. However, this reaction forms a do-nothing cycle of no net consequence. Protonated nitric acid is chemically equivalent to hydrated NO_2^+ , i.e., $\text{H}_2^+\text{NO}_3 \equiv \text{NO}_2^+\cdot\text{H}_2\text{O}$. When NO_2^+ is further hydrated it reacts with water to produce HNO_3 and PH's,



a reaction analogous to (1), occurring at a lower hydration primarily because of the higher ionization potential of NO_2^+ as compared to NO .

It has been found⁸ that N_2O_5 , predicted theoretically to also occur in the ppb range in the stratosphere, has a behavior similar to that of nitric acid, i.e., reaction but no net effect. The reaction is



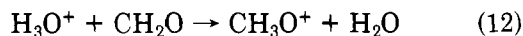
It is also known theoretically that formaldehyde exists in the stratosphere, as the first relatively long-lived (a few hours) reaction product of methane oxidation. The proton affinity of CH_2O exceeds that of H_2O slightly, by about 4 kcal mol^{-1} . This is insufficient to energet-

(7) F. C. Fehsenfeld, C. J. Howard, and A. L. Schmeltekopf, *J. Chem. Phys.*, **63**, 2835 (1975).

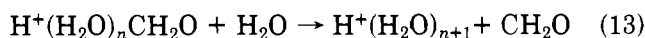
(6) I. Dotan, J. A. Davidson, F. C. Fehsenfeld, and D. L. Albritton, *J. Geophys. Res.*, **83**, 5036 (1978).

(8) J. A. Davidson, A. A. Viggiano, C. J. Howard, I. Dotan, F. C. Fehsenfeld, D. L. Albritton, and E. E. Ferguson, *J. Chem. Phys.*, **68**, 2085 (1978).

ically offset the greater affinity of H_3O^+ for additional water molecules compared to protonated formaldehyde. The reaction



is fast, $k_{12} = 2.2 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$, but upon further hydration reaction of the PH's with CH_2O becomes endothermic and the reverse reactions



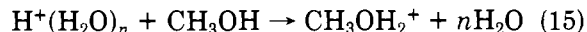
become exothermic and fast.⁹ Therefore even if protonated formaldehyde were produced in a moist atmosphere it would convert to PH's and not be detected. HNO_3 , N_2O_5 , and CH_2O are the known species in the stratosphere having proton affinities greater than water. There could be very many more, of course, in the sub part per trillion range, and the prospect of discovering such species adds great interest to the stratospheric ion observations.

One such species that might occur is NH_3 . Ammonia is known to be produced in the biosphere and to exist in the lower troposphere, but it is presumed to be removed in the troposphere because of its solubility in water without reaching the stratosphere. The proton affinity of NH_3 greatly exceeds that of H_2O , and the reactions



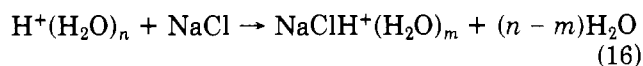
are known¹⁰ to be fast for $n \leq 4$ (and presumably for $n > 4$ as well, although the measurements extend only to 4).

Another species found⁹ to be reactive is methanol

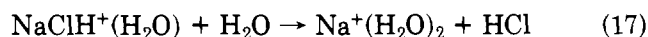


CH_3OH might conceivably arise from methane oxidation, although most methane oxidation schemes do not suggest this.

Several metallic compounds have large proton affinities; e.g., $\text{PA}(\text{NaOH}) = 250 \text{ kcal mol}^{-1}$, $\text{PA}(\text{NaCl}) = 213 \text{ kcal mol}^{-1}$, $\text{PA}(\text{NaNO}_3) \gg 170 \text{ kcal mol}^{-1}$, $\text{PA}(\text{MgO}) > 207 \text{ kcal mol}^{-1}$, $\text{PA}(\text{MgOH}) \gg 170 \text{ kcal mol}^{-1}$. The metals Na, K, and Mg have been observed in the D region by optical means. The metal ions Mg^+ , Fe^+ , Na^+ , K^+ , and many more, and also Si^+ , have been observed by rocket-borne mass spectrometers. The metals arise from meteor ablation in the earth's atmosphere. If sodium exists in the gas phase in the stratosphere, it would certainly react with PH's and show up in the ion chemistry.¹¹ Independently of the form of the Na, it would appear as protonated NaOH (hydrated Na^+).¹¹ For example, if Na were present as NaCl, reaction 16 would occur,



and then be followed by



and similar reactions for different values of m since

(9) F. C. Fehsenfeld, I. Dotan, D. L. Albritton, C. J. Howard, and E. E. Ferguson, *J. Geophys. Res.*, **83**, 1333 (1978).

(10) F. C. Fehsenfeld and E. E. Ferguson, *J. Chem. Phys.*, **59**, 6272 (1973).

(11) R. A. Perry, B. R. Rowe, A. A. Viggiano, D. L. Albritton, E. E. Ferguson, and F. C. Fehsenfeld, *Geophys. Res. Lett.*, **7**, 693 (1980).

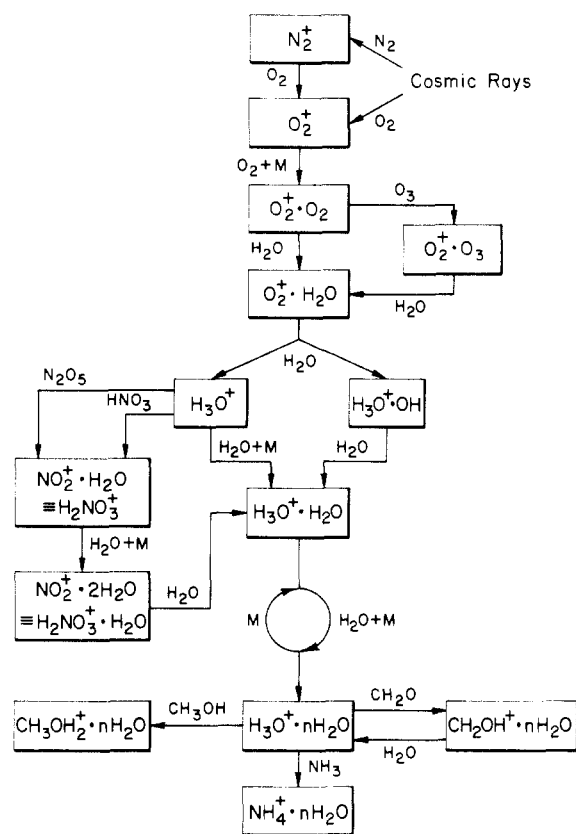


Figure 2. Stratospheric positive ion reaction scheme. (Reproduced with permission from ref 1. Copyright 1979, Academic Press.)

$\text{NaClH}^+ \equiv \text{Na}^+\text{HCl}$. The measured dissociation energy $D(\text{Na}^+ - \text{H}_2\text{O}) = 24.0 \text{ kcal mol}^{-1}$ exceeds $D(\text{Na}^+ - \text{HCl}) = 12.2 \text{ kcal mol}^{-1}$ so that H_2O molecules will displace HCl molecules clustered to Na^+ ions.¹¹ In a similar way NaNO_3 would abstract protons from PH's to produce NaNO_3H^+ ions which are equivalent to $\text{Na}^+\cdot\text{HNO}_3$ cluster ions, and since $D(\text{Na}^+ - \text{H}_2\text{O}) > D(\text{Na}^+ - \text{HNO}_3) = 21 \text{ kcal mol}^{-1}$, and the concentration of H_2O exceeds that of HNO_3 by a factor of 10^3 , the $\text{Na}^+\cdot\text{HNO}_3$ ions would be replaced by $\text{Na}^+\cdot\text{H}_2\text{O}$ ions. If NaOH were present it would directly abstract a proton from PH's to produce $\text{NaOH}\cdot\text{H}^+ \equiv \text{Na}^+\cdot\text{H}_2\text{O}$. The stratospheric positive ion scheme which has resulted from laboratory studies of ion molecule reactions is shown in Figure 2.

The first stratospheric positive ion composition measurements were made in 1972 by using a rocket-borne mass spectrometer.¹² It was found in these measurements, which extended to an altitude as low as 35 km, that PH's were dominant ions. An upper limit of $\sim 10^5 \text{ cm}^{-3}$ was placed on the total concentration above $\sim 40 \text{ km}$ of certain compounds which irreversibly react with PH's, including NH_3 , CH_3OH , NaOH , NaCl , NaNO_3 , MgO , and MgOH (also cf. ref. 13). Besides PH's, however, other ion species termed NPH's (non proton hydrates) were detected. It was found that the total fractional abundance of NPH's increases with decreasing altitude from about 0.01–0.1 at 50 km to about 0.2–0.8 around 40 km (Figure 3). Subsequent rocket measurements essentially confirmed this finding, but they could not identify the nature of the NPH's.

(12) F. Arnold, D. Krankowsky, and K. H. Marien, *Nature (London)*, **267**, 30 (1977).

(13) F. Arnold, H. Bohringer, and G. Henschen, *Geophys. Res. Lett.*, **5**, 653 (1978).

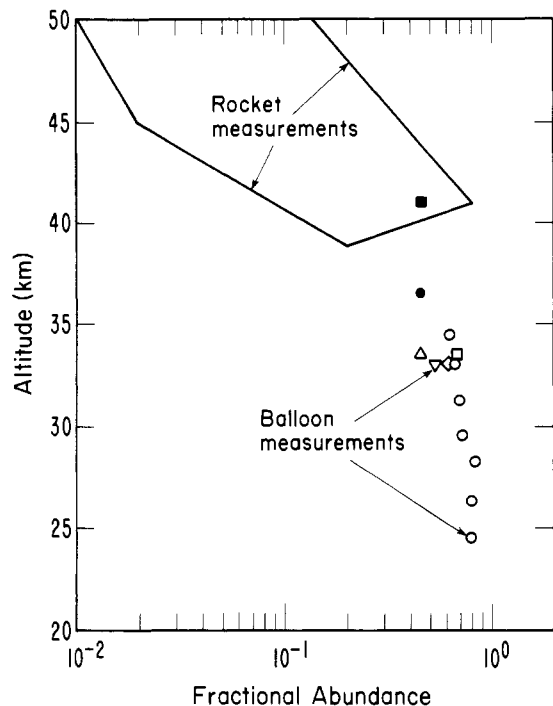


Figure 3. Fractional abundance of non proton hydrate ions as measured by rocket (enclosed area) and balloon-borne ion mass spectrometers.

Improved stratospheric positive ion composition measurements, using balloon platforms, were made for the first time in 1977 by the Heidelberg group¹³ and by Arijis and colleagues¹⁴ at the Institute for Space Aeronomy (Brussels). These measurements reached much higher sensitivity and mass resolution, but they were restricted to the altitude range near 35 km. The total fractional abundance of NPH's observed is consistent with the rocket results (Figure 3), and the major NPH's were found to have masses of 78 ± 1 , 96 ± 1 , 101 ± 1 , and 119 ± 1 amu (atomic mass units). As noted by Arnold et al.,¹³ the NPH's have the general form $H^+(X)_1(H_2O)_m$. Initially the mass of X was uncertain, 41 ± 1 amu.

It was proposed¹⁵ that X might be NaOH. Liu and Reid¹⁶ showed that if the meteoric sodium were in the gas phase in the stratosphere, the concentration would be sufficient to convert PH's to NPH's containing sodium. Higher resolution mass spectra have recently shown^{17,18} that the mass of X is 41, and therefore NaOH is eliminated as a possibility. The mass spectra also indicate that X is not MgOH because the ²⁵Mg and ²⁶Mg isotopes do not appear in the $H^+X_1(H_2O)_m$ ion.

It also has been shown that if meteoric sodium remained in the gas phase from 90 km down into the stratosphere, Na-containing NPH's would dominate the PH's everywhere below ~ 80 km. The inescapable conclusion appears to be that the sodium, and presumably the other less volatile meteor ablation products, are in a condensed aerosol or particulate phase below ~ 80 km.¹⁷ This is consistent with recent theoretical

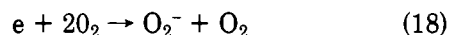
analyses^{19,20} of aerosol formation, although the detailed mechanism of condensation is poorly understood. The ion composition measurements thus contribute to our knowledge of atmospheric aerosol. The only current suggestion for the identity of X is acetonitrile,¹³ CH_3CN , which has the proper mass and a large proton affinity. A source of stratospheric CH_3CN has not yet been identified.

Recently, the Heidelberg group extended balloon-borne stratospheric positive ion composition measurements over a large height range from about 14 km to 42 km.^{21,22} It was found that NPH's are present throughout this range. Their total fractional abundance down to 24 km is shown in Figure 3. PH's are also present at heights at least as low as 25 km, which places an upper limit of about 3×10^{-12} volume mixing ratio to the abundance of compounds which irreversibly react with PH's at that altitude. Recently, the detection limit of stratospheric ion composition measurements was lowered, which resulted in the detection of a number of new NPH species also containing molecules other than X.²³

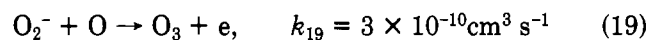
Stratospheric Negative Ions

As in the case of the positive ion chemistry, the stratospheric negative ion chemistry is treated as an extension of D-region ion chemistry. In the D region, the observations are far fewer for negative ions than for positive ions. The observed ion composition is highly variable. The negative ion composition is very dependent on trace species (such as O, NO, O₃, and H) whose concentrations are highly variable in altitude and time. Our understanding of negative ion chemistry is incomplete. However, many laboratory reaction rates have been measured, and detailed reaction schemes have been produced. The D-region schemes lead to NO₃⁻ and its hydrates as terminal ions, and they are indeed often observed to be the most abundant negative ions.

As in the case of the positive ions, an extension of D-region to stratospheric ion chemistry involves the same two questions: (1) will NO₃⁻ still be produced as a terminal negative ion? If so, (2) will NO₃⁻ further react with trace stratospheric species to produce more stable negative ions? Again, as in the case of the positive ions, the answers to both questions appear to be yes. In the case of NO₃⁻ production it is greatly facilitated in the stratosphere relative to the D region. In both regions, negative ion chemistry is initiated by electron attachment to O₂,



In the D region, stable negative ion production is hindered by atomic oxygen reactions, by associative detachment,



and by charge transfer

(19) R. P. Turco, O. B. Toon, P. Hamill, and R. C. Whitten, *J. Geophys. Res.*, **86**, 1113 (1981).

(20) D. M. Hunten, R. P. Turco, and O. W. Toon, *J. Atmos. Sci.*, **37**, 1342 (1980).

(21) G. Henschen and F. Arnold, *Geophys. Res. Lett.*, submitted for publication.

(22) G. Henschen and F. Arnold, *Planet. Space Sci.*, submitted for publication.

(23) G. Henschen and F. Arnold, *Nature (London)*, in press.

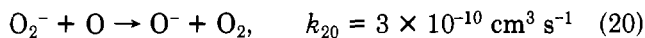
(14) E. Arijis, J. Ingels, and D. Nevejans, *Nature (London)*, **271**, 642 (1978).

(15) E. E. Ferguson, *Geophys. Res. Lett.*, **5**, 1035 (1978).

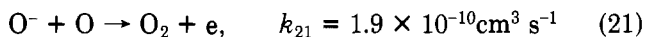
(16) S. C. Liu and G. C. Reid, *Geophys. Res. Lett.*, **6**, 283 (1979).

(17) F. Arnold, G. Henschen, and E. E. Ferguson, *Planet. Space Sci.*, **29**, 185 (1981).

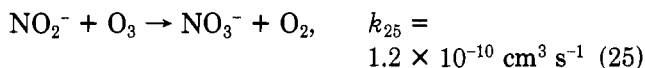
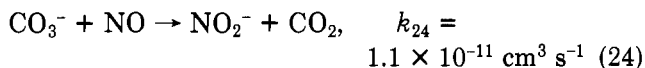
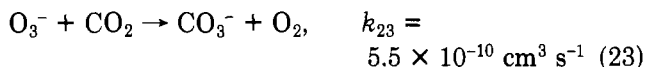
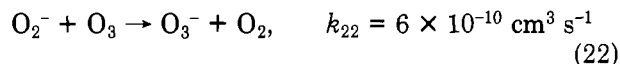
(18) E. Arijis, D. Nevejans, and J. Ingels, *Nature (London)*, **288**, 684 (1980).



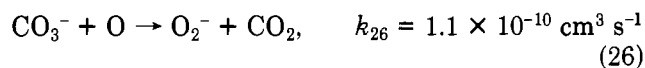
The O^- ion is destroyed by associative detachment with atomic oxygen



The NO_3^- ion is produced mainly by a reaction sequence

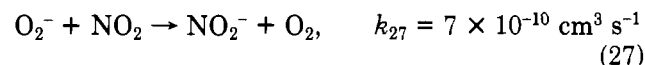


CO_3^- is a serious bottleneck to NO_3^- production because of the low NO concentration and low rate constant and because CO_3^- is destroyed by atomic oxygen,



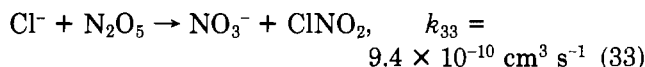
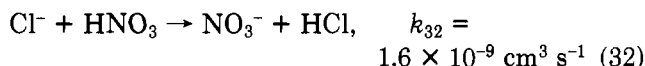
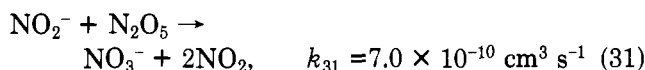
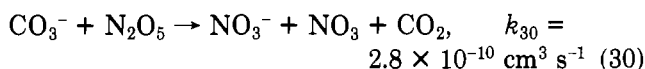
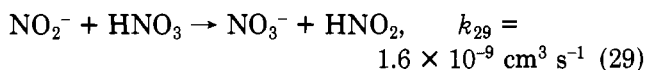
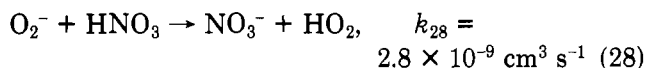
The NO concentration is highly variable in the D region, and this is undoubtedly partially responsible for a large variability which is observed in D-region negative ion composition measurements.

In the stratosphere, there is no appreciable O atom concentration to interrupt the sequence. In addition, the NO_2 concentration is quite large and the fast reaction



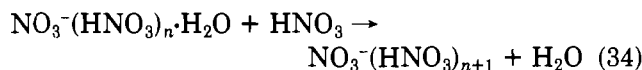
leads directly to NO_2^- , which rapidly converts to NO_3^- because of the large O_3 concentration in the stratosphere.

Moreover, the large (several ppb) concentrations of HNO_3 and N_2O_5 lead directly to NO_3^- production by reaction with O_2^- , O_3^- , CO_3^- , and NO_2^- , e.g.



and other reactions.⁸ It seems quite clear that NO_3^- will indeed be produced in the stratosphere.

Any atmospheric positive or negative ion will rapidly hydrate. Hydration is due to the charge-dipole electrostatic interaction and is not highly specific as to ions. However, in the stratosphere, nitric acid displaces water clustered to negative ions,



These reactions (for small n such as will occur in the atmosphere) are exothermic and fast.⁷ The equilibrium constants, $\geq 10^5$, exceed the $[\text{H}_2\text{O}]/[\text{HNO}_3]$ ratio, $\sim 10^3$, so that only small fractional concentrations of hydrated ions occur.

The question of the stability of $\text{NO}_3^-(\text{HNO}_3)_n$ ions against reaction is determined by the energetics of possible reactions with trace species. The electron affinity²⁴ of NO_3 is 4.01 eV, and this is increased by HNO_3 solvation, roughly ~ 1 eV per HNO_3 for small n . This leads to very large effective electron affinities. It is not likely that any species exists in the atmosphere with an electron affinity as large as this that could allow direct electron transfer.

The first stratospheric negative ion composition measurements, obtained by Arnold and Henschen²⁵ using a balloon-borne mass spectrometer around 35 km, indeed confirmed the presence of the expected NO_3^- (HNO_3)_{*n*} ions. However, $\text{HSO}_4^-(\text{H}_2\text{SO}_4)_j(\text{HNO}_3)_k$ ions were also detected in comparable abundance. Subsequent measurements of the Heidelberg²⁶ and Brussels groups,²⁷ made at the same height, essentially confirmed the initial findings and provided evidence for the dominance of rather massive $\text{HSO}_4^-(\text{H}_2\text{SO}_4)_n$ ions which, due to the limited mass range of the initial measurements, could not be detected before. The negative ion reaction scheme also including the $\text{HSO}_4^-(\text{H}_2\text{SO}_4)_n$ -(HNO_3)_{*m*} ions is shown in Figure 4.

Recently, as for positive ions, the Heidelberg group obtained the first measurements of the height variation of the stratospheric negative ion composition between about 23 and 39 km using balloon-borne mass spectrometers.²⁸ It was found that cluster ions containing NO_3^- cores dominate below about 30–35 km and that cluster ions containing HSO_4^- cores dominate above this height. The transition from the NO_3^- to the HSO_4^- regime is very abrupt, occurring within a few kilometers (Figure 5). It has been suggested that this abrupt transition is due to the steep increase of the sulfuric acid vapor concentration around 30–35 km which will be discussed later on.

Since, as suggested by Arnold and Henschen²⁵ and confirmed by laboratory measurements of Viggiano et al.,²⁹ H_2SO_4 reacts with NO_3^- core ions to form ions with HSO_4^- cores, the H_2SO_4 concentration can be inferred from the negative ion composition measurements. Thus, negative ion composition measurements are a powerful tool for probing this important stratospheric trace gas, which had not previously been detected in the stratosphere. Its importance is due to the fact that it is the most important nucleating agent in the stratosphere and thus is responsible for the formation of the stratospheric aerosol layer ("Junge layer"). This aerosol layer influences the earth's albedo and therefore has the

(24) J. A. Davidson, F. C. Fehsenfeld, and C. J. Howard, *Int. J. Chem. Kinetics*, **9**, 17 (1977).

(25) F. Arnold and G. Henschen, *Nature (London)* **257**, 521 (1978).

(26) F. Arnold, R. Fabian, E. E. Ferguson, and W. Joos, *Planet. Space Sci.*, **29**, 195 (1981).

(27) E. Arijs, D. Nevejans, P. Frederick, and J. Ingels, *Geophys. Res. Lett.*, **8**, 121 (1981).

(28) A. A. Viggiano and F. Arnold, *Geophys. Res. Lett.*, **8**, 583 (1981).

(29) A. A. Viggiano, R. A. Perry, D. L. Albritton, E. E. Ferguson, and F. C. Fehsenfeld, *J. Geophys. Res.*, **85**, 4551 (1980).

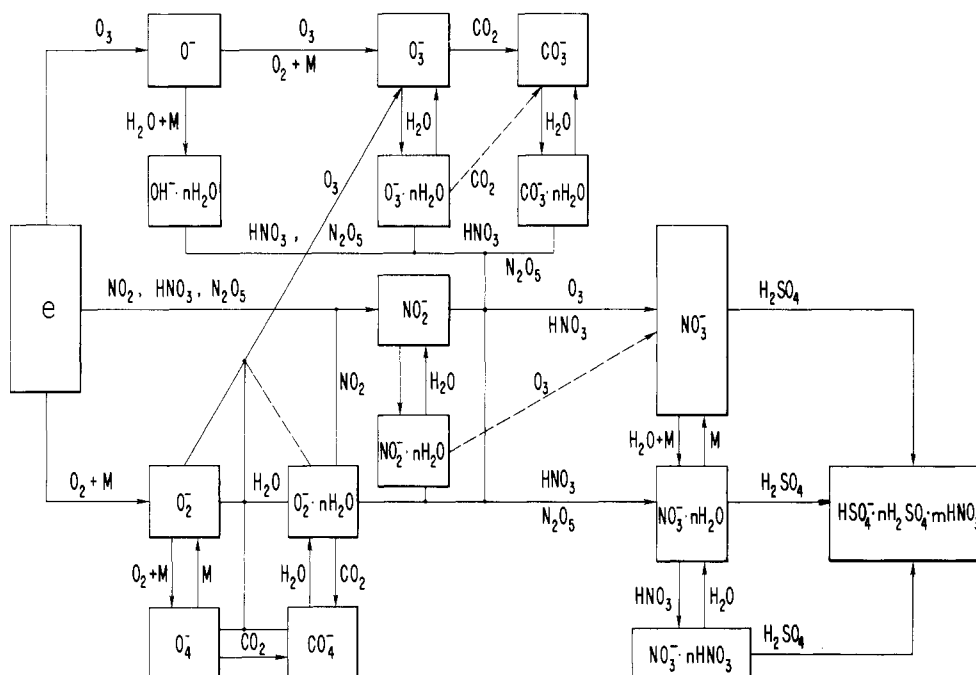


Figure 4. Stratosphere negative ion reaction scheme. (Reproduced with permission from ref 1. Copyright 1979, Academic Press).

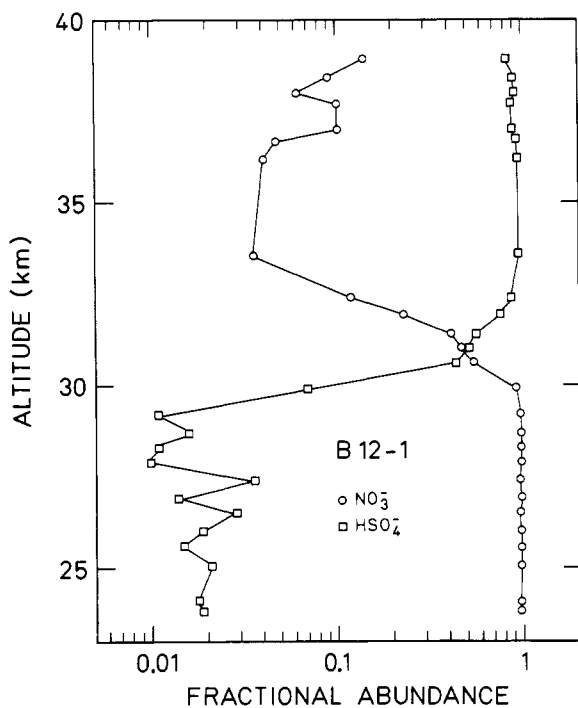
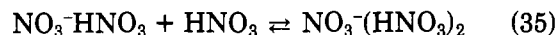


Figure 5. Fractional abundances of negative ions containing NO_3^- and HSO_4^- cores. (Reproduced with permission from ref 28. Copyright 1981, Pergamon Press.)

potential for climatic influences on earth. The measurements reveal that the H_2SO_4 vapor concentration increases steeply around 30 km to a maximum of about 10^7 cm^{-3} around 35 km. The steep rise is due to a corresponding increase of the H_2SO_4 -saturation pressure over the aerosol which is induced by a rise of temperature. In the region between about 27 and 35 km the sulfuric acid vapor partial pressure is equal to the saturation pressure. The measured partial pressure is consistent with the idea that the aerosol consists of H_2SO_4 - H_2O solution droplets with mass fractions of about 75% H_2SO_4 and 25% H_2O . Thus, the ion composition data provide important information on the

nature of the stratospheric aerosol.

Another important trace gas whose abundance was inferred from negative ion composition measurements is nitric acid. The HNO_3 molecule represents the major unreactive reservoir for the stratospheric odd nitrogen compounds which catalytically remove ozone and is therefore of great interest. Since the observed ions $\text{NO}_3^- \cdot \text{HNO}_3$ and $\text{NO}_3^- (\text{HNO}_3)_2$ are in near equilibrium



the concentration of HNO_3 can be determined from the measured ion abundances by using thermodynamic data obtained from laboratory measurements. Using the laboratory data of Davidson et al.,²⁴ Arnold and colleagues³⁰ determined the HNO_3 abundance from their stratospheric ion composition measurements. The resulting value is ~ 1 ppb at 36.5 km.

Recently, the detection limit for stratospheric negative ion measurements has been lowered to 1 ion cm^{-3} , and a number of minor ion species was detected by the Heidelberg group.³¹ Among these are NO_3^- and NO_3^- hydrates which, as initially suggested by Arnold et al.,³⁰ offers the possibility of inferring more precise HNO_3 abundances from stratospheric ion composition measurements. Finally, large negative ions with masses exceeding several hundred have been observed in the stratosphere but not yet identified.

Concluding Remarks

The recent progress in stratospheric ion chemistry has been significant. Further measurements, which have only recently become technically feasible, promise to shed additional light on atmospheric reaction processes, atmospheric nucleation processes, and atmospheric concentrations of certain trace species. Eventually these measurements will be extended into the troposphere. It is a remarkable fact that we do not at

(30) F. Arnold, R. Fabian, G. Henschen, and W. Joos, *Planet. Space Sci.*, 28, 681 (1980).

(31) L. McCrumb and F. Arnold, *Nature (London)*, submitted for publication.

present know the nature of the positive and negative ions in the air around us. Their concentration, $\sim 10^3 \text{ cm}^{-3}$, is about the same as the ion concentration in the stratosphere, and for that matter, about the same as the D-region ion density. The ion density is not greatly different from 80 km to the surface of the earth. Measurements of the tropospheric ions should provide

us with a remarkably sensitive determination of at least two trace neutrals, one in the positive ions and one in the negative ions, and perhaps more. Possibly the ion composition will be variable as the critical species (as determined largely by energetics) vary with time, especially if anthropogenic pollutants turn out to be involved.

Collision-Induced Energy Flow between Vibrational Modes of Small Polyatomic Molecules

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There is considerable fundamental and practical interest in determining the rates and mechanisms for collision-induced intermode energy flow in polyatomic molecules. Since the potential surfaces for the collisional interactions of polyatomic molecules are necessarily complex, such data serve as a guide and test for approximate theoretical models. In addition a knowledge of such rates and mechanisms can be used to influence the course of chemical reactions or to develop new laser systems.

The advent of monochromatic, intense, short-pulse infrared laser systems¹ provided an extremely convenient means for studying vibrational energy transfer via time-resolved infrared fluorescence techniques.^{2,3} The application of these methods to the study of intermode energy transfer in small, rigid polyatomics has led to a considerable body of experimental data which provides a fairly detailed picture of collision-induced energy flow in at least a small number of molecular systems.⁴⁻⁶ Some of the physical and chemical features which determine the rates and mechanisms for energy transfer in these molecules are now evident.

A detailed kinetic description of the energy-transfer processes which couple all vibrational states of energy less than (e.g.) 3000 cm^{-1} is enormously complex even for a triatomic. The number of kinetic rate constants required to describe fully such a system of n levels can be shown to scale like $n(n-1)/2$.^{7,8} Thus even for a molecule with 10 levels of energy less than this arbitrarily chosen value of 3000 cm^{-1} , 45 independent rate constants and hence 45 independent pieces of data are required to completely characterize the energy-transfer kinetics! Fortunately, the situation is not as grim as it might seem. In fact, for a significant number of small, rigid polyatomics a few rate constants are of overwhelming importance in determining the energy flow mechanism while most of the remaining kinetic pa-

rameters are of minimal importance. When stated in the language of cross sections, this simply means that only a handful of kinetic collision events have "sizeable" cross sections. Because of this feature, a great deal of insight into polyatomic molecule energy flow mechanisms can be obtained from the rather simple models.

A Minimum Model for Vibrational Relaxation of Small Molecules

Consider the block diagram of Figure 1. Here each vibrational mode for a triatomic has been represented by a single reservoir (box) which is in turn coupled to the other vibrational modes or reservoirs by a single channel. In addition only the lowest vibrational mode is coupled, again by a single channel, to the reservoir which represents the translational and rotational degrees of freedom. Though oversimplified, this model picture provides a great deal of physical insight into vibrational energy-transfer processes for small molecules. There are several reasons why this representation is a reasonable one, as will be demonstrated now with the molecule CH_3F as an example.

Why can all the states in a single mode be lumped into a single reservoir? This arises because the successive overtones of a given mode are rapidly coupled by kinetic events which are generally referred to as ladder-climbing processes. For example, if the vibrational mode ν_3 (1048 cm^{-1}) of CH_3F is pumped by a short pulse CO_2 laser

laser pump



(1) M. A. Kovacs, G. W. Flynn, and A. Javan, *Appl. Phys. Lett.*, **8**, 62 (1966); G. W. Flynn, M. A. Kovacs, C. K. Rhodes, and A. Javan, *ibid.*, **8**, 63 (1966); J. V. V. Kasper and G. C. Pimental, *Phys. Rev. Lett.*, **14**, 352 (1965).

(2) L. O. Hocker, M. A. Kovacs, C. K. Rhodes, G. W. Flynn, and A. Javan, *Phys. Rev. Lett.*, **17**, 233 (1966).

(3) C. B. Moore, R. E. Wood, B. B. Hu, and J. T. Yardley, *J. Chem. Phys.*, **46**, 4222 (1967); J. T. Yardley and C. B. Moore, *ibid.*, **46**, 4491 (1967).

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(5) E. Weitz and G. Flynn, *Annu. Rev. Phys. Chem.*, **25**, 275 (1974).

(6) E. Weitz and G. Flynn, *Adv. Chem. Phys.*, **47**, 185-235 (1981).

(7) See, for example, J. T. Yardley, "Introduction to Molecular Energy Transfer", Academic Press, New York, 1980.

(8) R. S. Sheorey and G. W. Flynn, *J. Chem. Phys.*, **72**, 1175 (1980).

George Flynn (born in Hartford, CN, in 1938) received his B.S. degree in Chemistry from Yale University and his Ph.D. from Harvard University. After postdoctoral work in the Physics Department at M.I.T., he took a position in the Department of Chemistry, Columbia University, where he is now Professor and Director of the Columbia Radiation Laboratory. His research interests include laser studies of vibrational relaxation, vibrational energy disposal in photofragmentation processes, chemical reactions of vibrationally excited molecules, and energy relaxation in low-temperature rare gas matrices.